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K_2CO_3/hindered cyclic amine blend (SEFY-1) as a solvent for CO_2 capture from various industries

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Abstract

The solvent blend of potassium carbonate and hindered cyclic amines having higher solubility, 500g/L water at 25 ^oC, and boiling point over 150^{o}C, SEFY-1 (Save Earth's Future by Yoon), has been investigated as an alternative of alkanolamines such as MEA or AMP/PZ for CO_2 capture from power plants using coal and industries having exit CO_2 concentration below 28 vol%. SEFY-1 offers several advantages in comparison with previous solvents because of very low heat of absorption, low volatility, high resistance to thermal and reactive degradation by SO_2, so cheaper than KS-1 solvent, no formation of salts and a lot of application for various industries having different CO_2 feed concentration such as power plant (8~13%), steel (15~20%), cement (15~25%) and chemical industries.

We concluded many advantages of SEFY-1 by various experiment, vapor liquid equilbrium test, corrosion test, reaction calorimeter, wetted wall column test, unit operation of absorption tower and so on. Specially, the heat of absorption, 1.36 GJ/tCO_2, of SEFY-1 was analyzed by Mettler Toredo Reaction Calorimeter. This is innovative result in comparison with commercial solution, MEA 30wt% (1.93 GJ/tCO_2) and KS-1 (1.55 GJ/tCO_2).

Keywords : potassium carbonate solution, CO2, MEA, KS-1, CO2 capture

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1. Introduction

CO_2 is a main pollutant causing greenhouse effect, which makes various environmental disasters. Though many efforts to reduce CO_2 have been studied using various methods such as absorption, adsorption, membrane, biological treating, hydration and so on, absorption method is only suitable for large treating of it and commercially available method. Absorption method has been used commercially for a long time and proved for large scale process.

However, absorption methods using monoethanolamine, diethanolamine, 2-amino-2-methyl-1-propanol, methyldiethanolamine, diglycolamine, hindered amines, have the critical disadvantage that the regeneration energy consumption is high and there are many side reactions in spite of widely commercialization method.

Blends of primary and tertiary amines or secondary and tertiary amines make the synergetic effects that the higher absorption rate of primary or secondary amine with higher equilibrium capacity of tertiary amine. Glasscock et al. (1991) and Hagewiesche et al. (1995) studied CO_2 absorption rate into aqueous MDEA/MEA solutions. Xiao et al. (2000) and Mandal and Bandyopadhyay (2006) investigated CO_2 absorption into aqueous AMP/MEA solutions.

Aqueous potassium carbonate (K_2CO_3) solution is effective for treating synthesis gas at high temperature and pressure. Benson et al. (1954, 1956) tested performance of K_2CO_3 40 wt% solution in a pilot plant in order to determine the steam consumption for regeneration at various operating conditions. The higher temperature about 105~140^{o}C increases the solubility of K_2CO_3, thus permitting operation with high concentration. Estimated cost for removing CO_2 of the hot potassium carbonate solution was lower than that of aqueous alkanolamine solution. The Benfield process is an example of commercial process that uses a K_2CO_3 20-30 wt% solution and Rochelle (2004, 2006) studied thermodynamics and kinetics of aqueous K_2CO_3 solution promoted by piperazine (PZ). PZ has two amino groups, which favorable affect the absorption rate. K_2CO_3 1.8 m/PZ 1.8 m solution have absorption rate a factor of 1.5 higher than 7 m MEA at 333 K. But piperazine has a defect low solubility and formation of two liquid-liquid phase, if the composition between potassium carbonate and piperazine solution are more than the soluble point.

In this study, a cyclic diamine was examined as a potential addictive to solve the problems such as absorption rate, regeneration energy, solubility and chemical phase equilibrium. There is not existing literatures, discussing the reaction between K_2CO_3/hindered cyclic diamine and CO_2. The pK_a values of PZ were represented higher than MEA (Hamborg and Versteeg, 2009; Khalili et al., 2009). The cyclic diamine has a steric hindrance to reduce the regeneration energy, which is caused by forming an unstable carbamate, a large amount of bicarbonate and carbonate in solution. Therefore, the regeneration heat of hindered cyclie diamine is lower than PZ. And we tested the various CO_2 feed from 8~25% for assumption of industrial feeds. We named the K_2CO_3/hindered cyclic diamine solution as SEFY-1, which is a abbreviation of "Save Earth's Future by Yoon. Version 1" and the patent of this solution is pending for registration now.

2. Experiment

2.1. Solvent materials

The reagent grade of several alkanolamine solution, additive and promoter were obtained from Samjeon chemical reagent company. Aqueous solutions were prepared concentration of K_2CO_3 15, 20 wt%/hindered cyclic diamine 7.5, 10 wt%, K_2CO_3 15, 20 wt%/PZ 7.5, 10 wt%, respectively. Aqueous MEA and AMP solution was employed 30 wt%. PZ is a white solid at room temperature with solubility in water of 150 g/ℓ. Therefore, the K_2CO_3/PZ solution had to be heated before it was used in the experiment in order to obtain a solution with the preferred concentration. The CO_2 (purity 99.99%) and N_2 (purity 99.999%) gases were obtained from Special Gas Co. Ltd..

2.2. Verification of performance and experimental procedure

We tested and verified the performance of SEFY-1 by various experiment, vapor liquid equilbrium test, corrosion tester, reaction calorimeter, wetted wall column test, unit operation of absorption tower and so on. This equipment is listed in Fig. 1.

We tested SEFY-1 in comparison with several samples. The inlet CO_2 gas (99.99%) or mixed CO_2/N_2 gases were used for various tests. The procedure of tests are executed through 4th steps as follows ;

(1) CO_2 loading and absorption rate test : Vapor-Liquid Equilibrium (Shell and CSTR type reactor), Wetted wall column
(2) The absorption heat test : Reaction calorimeter, Differential reaction calorimeter
(3) Side reaction test : Corrosion tester, Electronic corrosion meter, Side reaction tester
(4) Continuous test : 10 Nm^3/h bench scale continuous unit

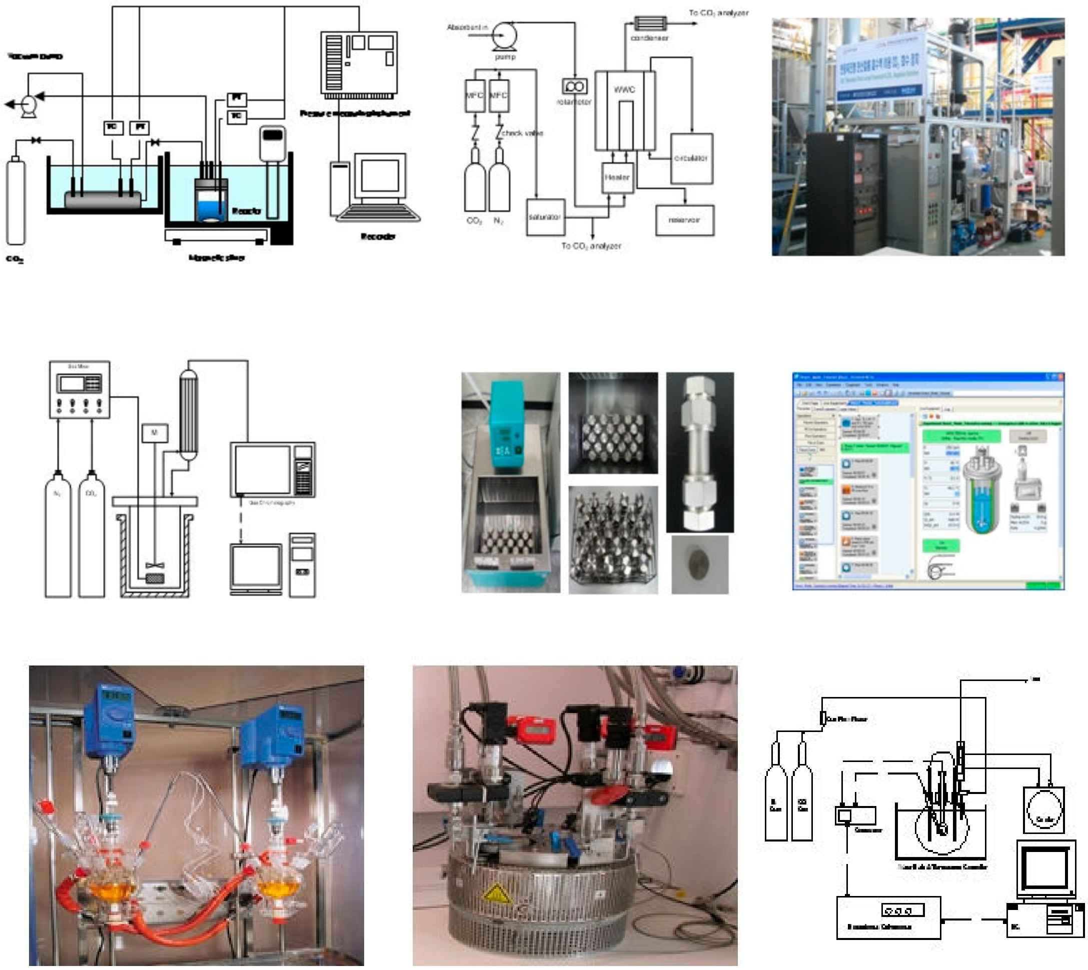

Figure. 1 The verification apparatus for absorbent (Vapor-Liquid Equilibrium, Wetted Wall column, 10 Nm^3/h bench scale continuous unit, CSTR type VLE, Corrosion tester, Reaction Calorimeter, Differential Reaction Calorimeter, Side Reaction Tester, Electronic Corrosion meter)

3. Results

3.1 Performance of absorption and regeneration

As the experimental results, SEFY-1 has many advantages in comparison with previous solvents. Especially, the heat of absorption per CO_2 loading,, this parameter is core parameter of absorbent with absorption velocity, was very lower than MEA. The heat of absorption, 1.36 GJ/tCO_2, of SEFY-1 was analyzed by Reaction Calorimeter. This is the innovative result in comparison with commercial solution, MEA 30wt% (1.93 GJ/tCO_2) and AMP/PZ (1.55 GJ/tCO_2). The regeneration heat of regeneration tower is made up of heat of reaction, sensible heat and latent heat. The heat of reaction is characteristic term and command an overwhelming majority of performance of chemical absorbent.

The absorption velocity of SEFY-1 is similar to MEA 30wt% as a test result by wetted wall column. This means that previous process using alkanolamine solution can be replaced by SEFY-1 due to similar absorption velocity.

Figure 2 shows that SEFY-1 has the no formation of salt and separation of chemical phase within the condition of patent. The salts by side reaction may cause the accident of closedown and chemical separation of absorbent may lower the process efficiency of make-up tank, absorber and stripper.

As an another merit of SEFY-1, this is not tested but scheduled this year, it has higher resistance than alkanolamine absorbent for side reaction with impurities such as sulfur dioxide, hydrogen chloride and halogens in the flue gases by previous research and commercial test results like Benfield process, which is reported that there is no salt formation of K_2SO_4 within 3%. This is very high value in comparison with MEA process , 15 ppm SO_2, and KS-1 process, 1 ppm SO_2.

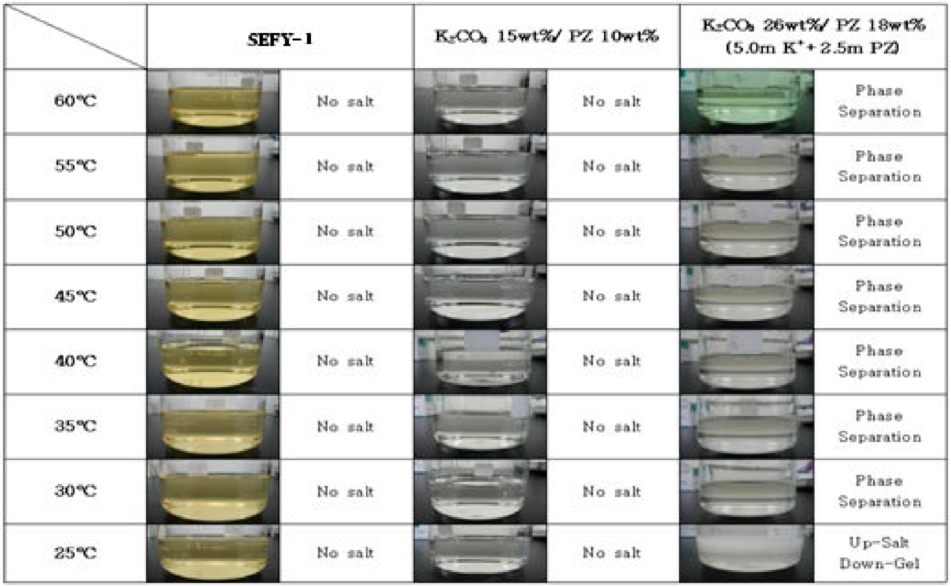

Figure 2. The chemical phase of SEFY-1 at various temperature

3.2 Performance of process

We could remove the CO_2 over 90~98% using the continuous process of bench scale, 10 Nm^3/h, connected with PC power plant, 2MW, using CFBC (Circulating Fluidized Bed Combustor) types in the Korea Institute of Energy Research. The CO_2 concentration of feed was 14 vol%. The CO_2 concentration of exit from absorber was 0.5~1 vol % over 3.5 at ratio of L/G and was 99.9~99.99 vol% at top of stripper. This CO_2 removing performance at higher CO_2 concentration was also attained. The Figure 3 shows that the conversion ratio in comparison with feed CO_2, 15~28%, was over 80~85% during 50 hours. This means that SEFY-1 can be utilized various industries except PC power plant.

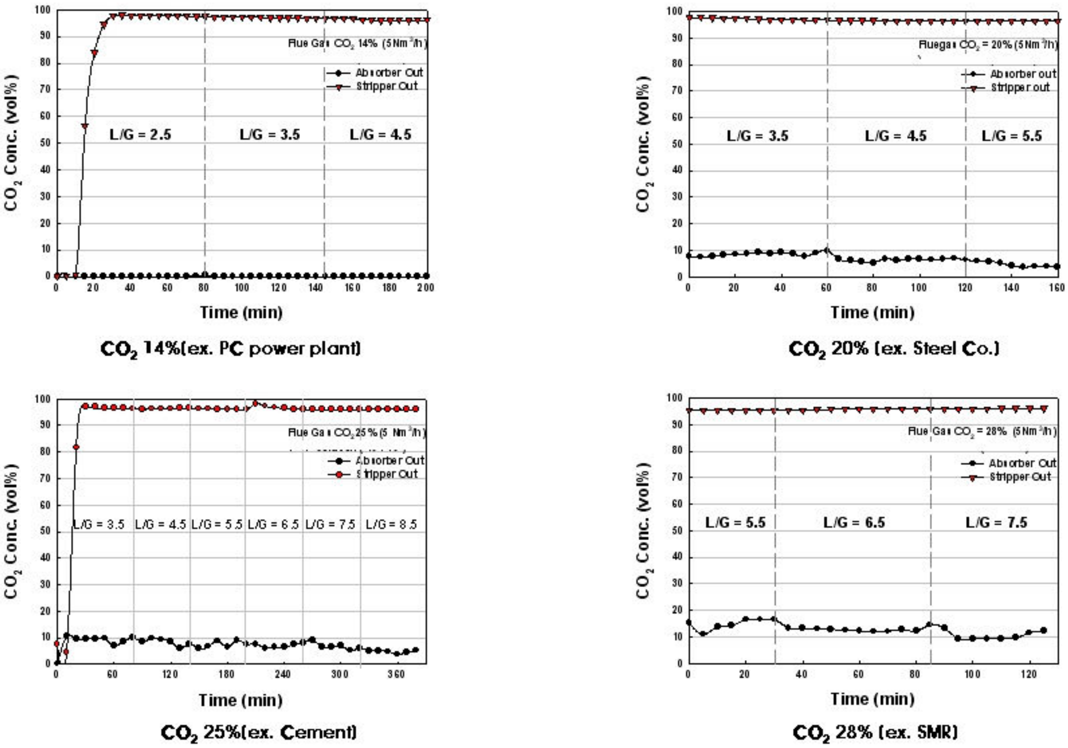

Figure. 3 Test results of SEFY-1 for various CO_2 concentration using bench scale unit

4. Conclusion

We concluded many advantages of SEFY-1 by various experiment, vapor liquid equilbrium test, corrosion test, reaction calorimeter, wetted wall column test, unit operation of absorption tower and so on. Specially, the heat of absorption of SEFY-1 was 1.36 GJ/tCO_2. This is innovative result in comparison with commercial solution, MEA 30wt% (1.93 GJ/tCO_2) and KS-1 (1.55 GJ/tCO_2). And cost of SEFY-1 is $3/kg at evaluation of commercial reagent sales, and so cheaper than commercial solution such as KS-1 ($ 16.5/kg). In addition to these advantages, SEFY-1 was just a little deactivated by SO_2 in spite of needing forced flue gas desulfurization about alkanolamine solutions, 15 ppm about MEA and 1 ppm about KS-1.

If SEFY-1 is improved and studied for more large scale unit, this will be the one of world best absorbent and can be replaced as a previous plant.

5. Acknowledgement

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